

THERMAL PROPERTIES OF CHITOSAN-PHOSPHAZENE POLYMERS

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The problems of the thermal properties of chitosan-phosphazene polymers containing different amounts of phosphazene units are discussed. Chitosan and microcrystalline cellulose are used for comparison. The chitosan-phosphazene polymers have lower temperatures of the maximum of the exothermic effect and of maximum mass-loss rate in comparison with those of chitosan. This is connected with degradation of the polymers, with subsequent pyrolysis to fragments which can inhibit flame.

Phosphazenes have been the subject of much interest as potential flame-retardants for several materials [1]. One approach to rendering materials (especially cellulose) fire-retardant is treatment with the aminopolysaccharide chitosan [2], followed by phosphazenylation [3]. Increase of the fire-resistance of materials by the addition of chitosan-phosphazene polymer is also possible.

One method for the correct estimation of the activity of such a flame retardant is thermal analysis [4].

This report is concerned with the thermal properties of phosphazene-chitosan polymers in the temperature range 20–500°.

Experimental

Thermal investigations were carried out on phosphazene-chitosan polymers containing different amount of phosphorus, obtained as described previously [3], the properties of which are given in Table 1, as well as on chitosan (Kypro Co., Seattle, Wa, USA) and microcrystalline cellulose ("Tomcel", ZWCh Chemitex-Wistom, Poland), which were used for comparison.

The thermal investigations were made with a derivatograph type OD-102 (MOM, Budapest, Hungary). In the case of DTA and TG, experiments were carried out with 100 mg samples. The determinations were performed in an atmosphere of air in the range of temperature 20–500° and at a heating rate of 5°/min.

Table 1

Physico-chemical properties of the chitosan-phosphazene polymers^a

Sample	Polymer type	NPCl ₂ oligomers used	Properties of solid product		Infrared absorption, frequency of units, cm ⁻¹	
			color	P content, %	P = N	P-N-C
A	chitosan-phosphazene	mixture	yellow	4.11	1250	950
B	chitosan-phosphazene	mixture	brown	5.80	1260	910
C	chitosan-phosphazene	mixture	brown	7.17	1245	960
D	chitosan-phosphazene	mixture	grey-yellow	8.44	1225	955
E	chitosan-phosphazene	trimer	grey	2.77	1230	930
F	chitosan-phosphazene	tetramer	light-brown	3.62	1260	—
G	chitosan-2-hydroxy-ethylaminophosphazene	mixture	grey	8.70	1265	910

The chitosan used for comparison had a MW of $1.3 \cdot 10^5$ and a deacetylation degree of 60%.

^a The polymers obtained in the reaction of chitosan and chlorophosphazenes or substituted chlorophosphazenes may contain a low amount of chlorine.

Results and discussion

Investigations of the thermal behaviour of materials having flame-resistant properties reveal the processes occurring on heat-treatment, the effectivity of flame-retardation and the quantity of flame-suppressant decomposition products evolved.

Figure 1 shows DTA curves of chitosan-phosphazene polymers and also of the chitosan and Tomcel cellulose used for comparison.

The thermal properties of the polymers studied are compared in Table 2.

From the DTA results (Fig. 1, Table 2) it may be stated that, in the case of chitosan-phosphazene polymers formed from a mixture of chlorophosphazene oligomers, an exothermic peak is observed in the temperature range 195–250°. The occurrence of this exothermic effect can be explained by the degradation of the chitosan-phosphazene polymer. The temperature of the maximum of the exothermic effect depends on the phosphazene unit content (characterized by the phosphorus concentration). Increase of the phosphazene amount (in products A–D) lowers the temperatures of both the maximum of the exothermic effect and the maximum mass-loss rate. At 500° the loss in mass is lower than that for chitosan (Table 2).

A small endothermic effect accompanies the distinct exothermic effect in the case of the highest phosphazene concentration (see D in Fig. 1 and Table 2). The endothermic effect may be explained by the probable difference in degradation process of this polymer, initiated at a lower temperature. A similar endothermic effect, interpreted by the beginning of degradation [5], is observed for chitosan.

Similar phenomena are found for the chitosan-phosphazene polymers obtained from chlorocyclotriphosphazene and octachlorocyclotetraphosphazene (E and F).

The maximum of the exothermic effect observed in the polymer formed by the hydroxyethylamino-phosphazenylation of chitosan (see G in Fig. 1 and Table 2)

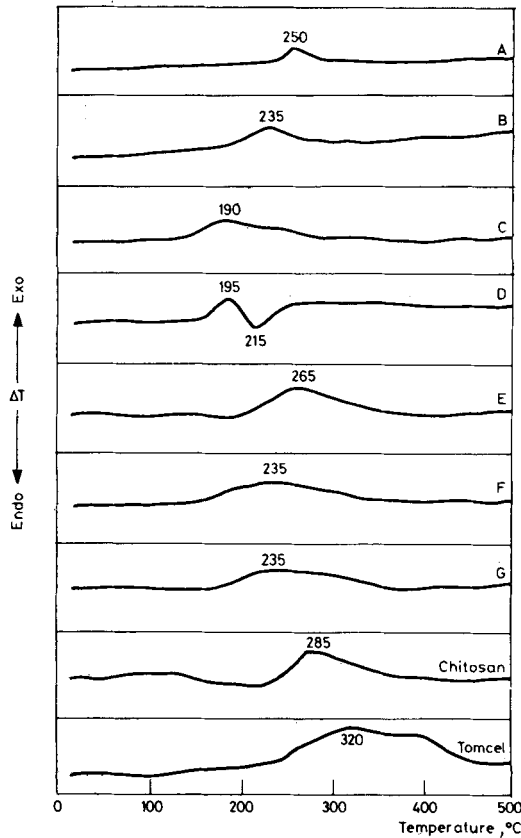


Fig. 1. DTA curves of: A–D – reaction products of chitosan and mixture of chlorophosphazene oligomers; E – reaction products of chitosan and hexachlorocyclotriphosphazene; F – reaction products of chitosan and octachlorocyclotetraphosphazene; G – reaction products of chitosan and 2-hydroxyethylaminochlorophosphazene; chitosan; and Tomcel microcrystalline cellulose

is at higher temperature than for the other products obtained from the same chlorophosphazene oligomers. This can be explained by the influence of the additional substituent in the phosphazene units on the thermal properties of this type of polymer.

In comparison with the chitosan and Tomcel microcrystalline cellulose, polymer discussed is characterized by lower temperatures of degradation and of maximum

Table 2

Thermal properties of chitosan-phosphazene

Sample	Phosphorus content, %	Temp. of endothermic effect, °C			Temp. of exothermic effect, °C		
		initial	max	end	initial	max	end
A	4.11	—	—	—	220	250	305
B	5.80	—	—	—	195	235	260
C	7.17	—	—	—	140	190	360
D	8.44	200	215	245	180	195	200
E	2.77	—	—	—	200	265	355
F	3.62	—	—	—	175	235	345
G	8.70	—	—	—	175	235	345
Chitosan	—	155	215	260	260	285	380
Tomcel	—	—	—	—	258	320	480

mass-loss rate. The degradation of this type of fire-retardant polymers is observed at relatively low temperature, yielding volatile, non-flammable, flame-inhibiting products. The lower temperature of the exothermic effect in comparison with that of chitosan is undoubtedly connected with the degradation of the chitosan-phosphazene derivative, with subsequent pyrolysis to fragments which can inhibit flame.

References

1. H. STRUSZCZYK, *Polimery*, 23 (1978) 41, 77.
2. R. A. MUZZARELLI, *Chitin*, Pergamon Press, New York, NY, 1977.
3. G. G. ALLAN, E. J. GILMARTIN and H. STRUSZCZYK, IUPAC Conference, Florence, Italy, 1980.
4. J. SIMON, Non-inflammability of Polymer Materials Conference, Strybske Pleso, Czechoslovakia, 1980.
5. M. BIHARI-VARGA, C. SEPULCHRE and E. MOCZAR, *J. Thermal Anal.*, 7 (1975) 675.

RÉSUMÉ — L'article discute le problème des propriétés thermiques d'un polymère chitosane-phosphazène contenant diverses quantités d'unités phosphazène dans sa structure. En même temps on s'est servi, pour comparaison, de chitosane et de cellulose microcristalline. Le polymère chitosane-phosphazène a montré une diminution de la température du maximum de l'effet exothermique et de la température du maximum de la vitesse de perte de masse, comparé au chitosane. Ce phénomène est en rapport avec la dégradation du polymère étudié ainsi qu'avec la pyrolyse des fragments formés dans ce processus qui joue comme inhibiteur de flamme.

ZUSAMMENFASSUNG — Es werden die Probleme der thermischen Eigenschaften eines Chitosan-Phosphazene-Polymers diskutiert, welches in seiner Struktur verschiedene Mengen von Phosphazeneinheiten enthält. Gleichzeitig wurden ein Chitosan und mikrokristalline Cellu-

polymers, chitosan and Tomcel

Temp. range of quick loss of mass, °C	Temp. of max. mass-loss rate, °C	Percentage of mass-loss at different temperatures				
		100°	200°	300°	400°	500°
180—265	240	6	11	20	24	32
195—245	225	4	8	22	26	30
170—245	200	5	14	24	27	31
180—255	195	3	10	19	22	28
200—290	255	6	8	25	29	33
185—255	230	6	8	24	28	32
170—245	200	4	10	21	24	27
230—300	280	3	11	22	27	39
168—345	285	3	5	27	37	47

lose zu Vergleichszwecken eingesetzt. Das Chitosan-Phosphazen-Polymer zeigte eine herabgesetzte Temperatur im Maximum des exothermen Effekts und eine Temperatur des Maximums der Geschwindigkeit des Massenverlustes im Vergleich zu Chitosan. Dieses Phänomen ist mit dem Abbau des Polymers verbunden sowie mit der Pyrolyse der in diesem Prozess gebildeten Fragmente, welche flammenhindernd sind.

Резюме — Обсуждены проблемы термических свойств хитозанфосфазен полимера с различным содержанием фосфазеновых цепей. В качестве образцов сравнения были использованы хитозан и микрокристаллическая целлюлоза. Хитозан-фосфазен полимер показал понижение температурного максимума экзотермического эффекта и температурного максимума скорости потери массы по сравнению с хитозаном. Это явление обусловлено распадом полимера, сопровождаясь в дальнейшем пиролизом фрагментов, образующихся в этом процессе, что может приводить к замедлению пламени.